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## **<sup>1</sup>H NMR STUDY OF 2,5-DIMETHYLRESORCINOL-METHYLOLPHENOL CO-CONDENSATION**

P. CHRISTJANSON

A. KÖÖSEL

A. SUURPERE

Tallinn Technical University  
Tallinn, Estonia

*Co-condensation of 2,5-dimethylresorcinol with ortho- and para-methylolphenols in the melt at 150 °C has been studied. 100 MHz <sup>1</sup>H NMR spectroscopy was used for evaluation the reaction kinetics and for the product identification. Low co-condensation rate with para-methylolphenol as compared to ortho-methylolphenol is the specific phenomenon of the reaction. The rate-determining role of 2,5-dimethylresorcinol reveals mainly in the co-condensation with para-methylolphenol.*

*The hydroxyl and methyl substituent effects are responsible for the resolution of co-condensate <sup>1</sup>H methylene signals. The co-condensation reaction occurs as the mono- and disubstitution of 2,5-dimethylresorcinol with methylol compound. The reaction with ortho-methylolphenol and particularly in the presence of alkaline catalyst enhances the part of 4,6-disubstitution in comparison with 4-monosubstitution.*

### **Introduction**

Co-condensation reaction of resorcinol with phenolic methylol oligomers can be regarded as the predominant reaction in the manufacture of phenol-resorcinol-formaldehyde adhesive resins. Most of weather-proof laminated timber constructions are produced using an adhesive of this type. A resin of similar quality has been synthesized substituting oil shale alkylresorcinols for the resorcinol. Oil shale alkylresorcinols contain about 50 % 5-methylresorcinol and up to 15 % 5-ethylresorcinol. The other prevailing components are disubstituted 2,5- and 4,5-dimethylresorcinols [1].

*Ortho*- and *para*-methylolphenols are the first-formed and most abundant compounds in phenol-formaldehyde reaction.  $^1\text{H}$  NMR study of their reaction with resorcinol and 5-methylresorcinol was successful in evaluating the reaction kinetics and for the product identification [2, 3]. By that the 5-methylresorcinol was specifically chosen since it is the most reactive resorcinol and the most abundant component of oil shale alkylresorcinols. 2,5-dimethylresorcinol, the other available constituent of oil shale alkylresorcinols, was used for this study. The characteristics of this resorcinol lie in its high melting point (161.5 °C), low solubility and reduced reactivity with formaldehyde. The latter is due to the opposite influence of *meta*- and *ortho*-methyl groups on the reactivity.

Following the principle of previously used melt-condensation [2, 3], the temperature of reaction should be raised to 150 °C due to the high melting point of 2,5-dimethylresorcinol. The difference in methylene  $^1\text{H}$  chemical shifts of *ortho*- and *para*-methylolphenol in pyridine (5.11 and 4.76 ppm, accordingly) allows us to follow the reaction kinetics also with equimolar mixture of methylols, giving really the possibility to follow the competition in the same mixture.

## Experimental

**Materials:** 2,5-Dimethylresorcinol (2,5DMR) was separated from oil shale alkylresorcinols at the Institute of Chemistry/Estonian Academy of Science (m.p. 161.5 °C, the content of main substance 98.4 %). *Ortho*-methylolphenol (*o*-MP) was recrystallized from benzene/ethyl alcohol (m.p. 84 °C) and *para*-methylolphenol (*p*-MP) from ethylacetate/hexane after the reduction from *p*-hydroxybenzaldehyde (m.p. 124 °C).

**Studied systems:** Molar ratios *o*-MP or *p*-MP/2,5DMR = 1/1 or 2/1 and *o*-MP/*p*-MP/2,5DMR = 1/1/2 or 1/1/1 were used. Reactions were carried out in the melt at 150 °C without catalyst and in the presence of 0.05 mole of NaOH, 0.005 mole of zinc acetate or 0.025 mole of benzoic acid.

**Analysis:** 100 MHz  $^1\text{H}$  NMR spectra were obtained to follow the reaction rate and to ascertain the product composition.  $^1\text{H}$  chemical shifts for samples in pyridine solution were measured from internal hexamethyldisiloxane and calculated from tetramethylsilane. Quantitative changes in molar concentrations during the reaction were calculated from integral intensities of the corresponding methylol and methylene signals.  $^1\text{H}$  chemical shifts of 2- and 5-methyl groups in 2,5DMR and in its compounds were also identified. Their amounts can be determined only on a more/less level.

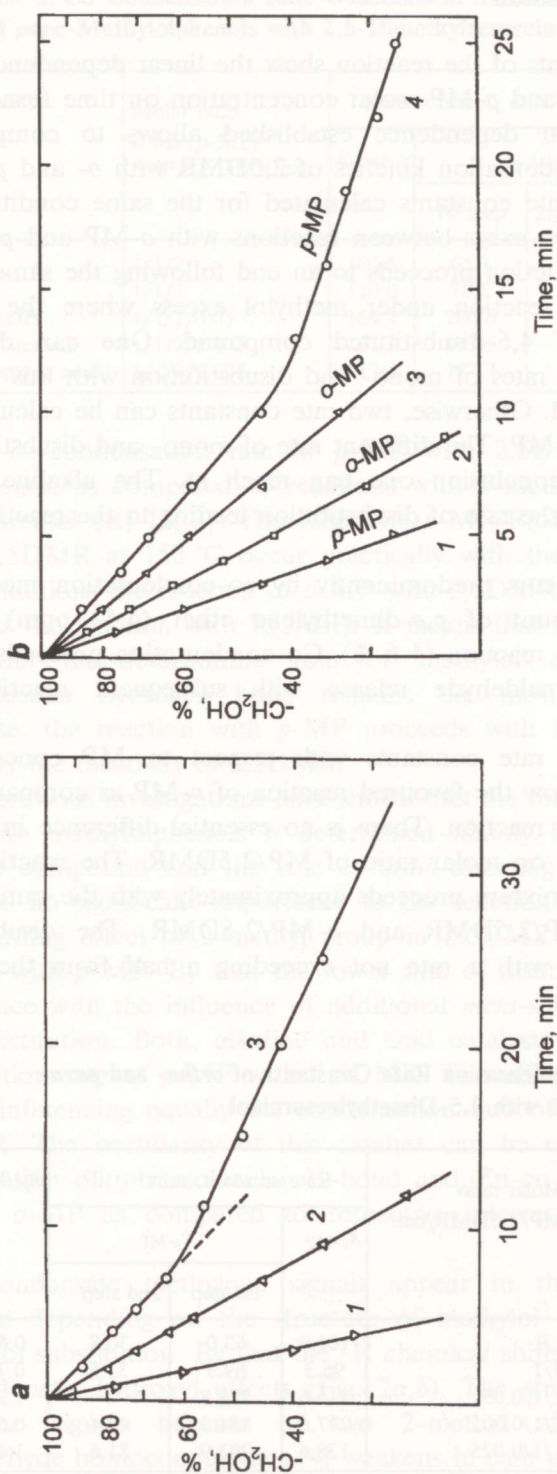


Fig. 1. Dependence of methylol content on reaction time. a: 1 - *p*-MP/2,5DMR/NaOH (1/1/0.05), 2 - *o*-MP/2,5DMR (1/1), 3 - *p*-MP/2,5DMR (1/1); b: 1 and 2 - *o*-MP/*p*-MP/2,5DMR/NaOH (1/1/2/0.05), 3 and 4 - *o*-MP/*p*-MP/2,5DMR (1/1/2)

## Results and Discussion

Kinetic measurements of the reaction show the linear dependence of the logarithm of *o*-MP and *p*-MP molar concentration on time (examples in Fig. 1). The linear dependence established allows to compare the complicated co-condensation kinetics of 2,5DMR with *o*- and *p*-MP by simple first order rate constants calculated for the same condition. The substantial difference exists between reactions with *o*-MP and *p*-MP. In the first case the reaction proceeds to an end following the same rate. It is so even in the reaction under methylol excess where the product consists mainly of 4,6-disubstituted compound. One can draw the conclusion that the rates of mono- and disubstitution with this methylol are practically equal. Otherwise, two rate constants can be calculated for the reaction with *p*-MP. The different rate of mono- and disubstitution is the only possible conclusion one can reach at. The alkaline catalyst influences stronger the rate of disubstitution leading to the reactions with equal rate constants.

The reaction occurs predominantly by co-condensation mechanism. Only a small amount of *p,p*-dimethylene ether (4.42 ppm) can be recorded during the reaction (4-6 %). Co-condensation proceeds without any signs of formaldehyde release with subsequent reaction with 2,5DMR.

The first order rate constants with respect to MP concentration (Tables 1 and 2) show the favoured reaction of *o*-MP as compared to *p*-MP in noncatalytic reaction. There is no essential difference in the rate constant depending on molar ratio of MP/2,5DMR. The reaction of *o*-MP and *p*-MP in mixture proceeds approximately with the same rate as compared to *o*-MP/2,5DMR and *p*-MP/2,5DMR. The disubstitution with *p*-MP occurs with a rate not exceeding a half from the rate of monosubstitution.

**Table 1. Co-Condensation Rate Constants of *ortho*- and *para*-Methylolphenols with 2,5-Dimethylresorcinol**

Catalyst	Molar ratio MP/2,5DMR/cat.	Rate constant, min <sup>-1</sup> · 10 <sup>3</sup>			<i>k<sub>pI</sub></i> / <i>k<sub>o</sub></i>
		<i>k<sub>o</sub></i> -MP	<i>k<sub>p</sub></i> -MP		
			1st step	2nd step	
-	1/1	101.9	63.0	30.8	0.62
-	2/1	96.3	69.3	31.5	0.72
NaOH	1/1/0.05	216.6	288.8	-	1.33
Zn acetate	1/1/0.005	247.6	154.0	44.4	0.62
Benzoic acid	1/1/0.025	138.6	203.9	81.6	1.47

Table 2. Co-Condensation Rate Constants of Mixture of *ortho*- and *para*-Methylolphenols with 2,5-Dimethylresorcinol

Catalyst	Molar ratio <i>o</i> -MP/ <i>p</i> -MP/ /MP/2,5DMR/cat.	Rate constant, min <sup>-1</sup> · 10 <sup>3</sup>			$k_{pI}/k_o$
		$k_{o\text{-MP}}$	$k_{p\text{-MP}}$		
			1st step	2nd step	
-	1/1/2	103.5	65.4	30.8	0.63
-	1/1/1	110.0	78.8	30.1	0.72
NaOH	1/1/2/0.05	169.1	266.6	-	1.58
Zn acetate	1/1/2/0.005	231.1	147.5	46.8	0.64
Benzoic acid	1/1/2/0.025	117.5	177.7	60.8	1.51

Low co-condensation rate of *p*-MP with 2,5DMR is the specific phenomenon as compared to reactions with 5-methylresorcinol (5MR) and resorcinol (R) [2, 3]. The reactions *p*-MP/R(5MR) at 120 °C and *p*-MP/2,5DMR at 150 °C occur practically with the same rate. In the same conditions the reaction of *o*-MP with 2,5DMR is about four times as fast as the reaction with R(5MR). It means that in the reaction with *o*-MP the rate-determining role of methylol compound due to intramolecular hydrogen bond remains the most important factor. Otherwise, the reaction with *p*-MP proceeds with the rate determined mainly by the reactivity of 2,5DMR.

Our previous investigations have shown that the reaction rate of R and 5MR with methylolphenols is determined mainly by the reactivity of methylol compound and the role of *ortho*-directing 5-methyl group in 5MR has no significant importance to the reaction rate [3]. The great rate-retarding effect of 2-methyl group in 2,5DMR reveals only in the reaction with *p*-MP. By that the lower rate of disubstitution is in good accordance with the influence of additional *meta*-substituent because of monosubstitution. Both, alkaline and acid catalysts enhance preferably the reaction rate of *p*-MP with 2,5DMR. The effective catalyst is zinc acetate influencing equally the condensation rate of *o*- and *p*-MP with 2,5DMR. The peculiarity of this catalyst can be explained by similar configuration of intramolecular H-bond and Zn-co-ordination bond in case of *o*-MP as compared to respective intermolecular bonds with *p*-MP.

Co-condensate methylene signals appear in the region of 4.23-4.54 ppm depending on the structure of methylol compound and the number of substitution. By that the <sup>1</sup>H chemical shifts are consistent with supposed *ortho*-hydroxyl effects (Fig. 2a,b). The strong upfield shift of methylene signals because of two 2-methyl effects in 2,5DMR formaldehyde homocondensates [4] weakens in case of co-condensates of 2,5DMR with methylol compounds. The co-influence of substituent

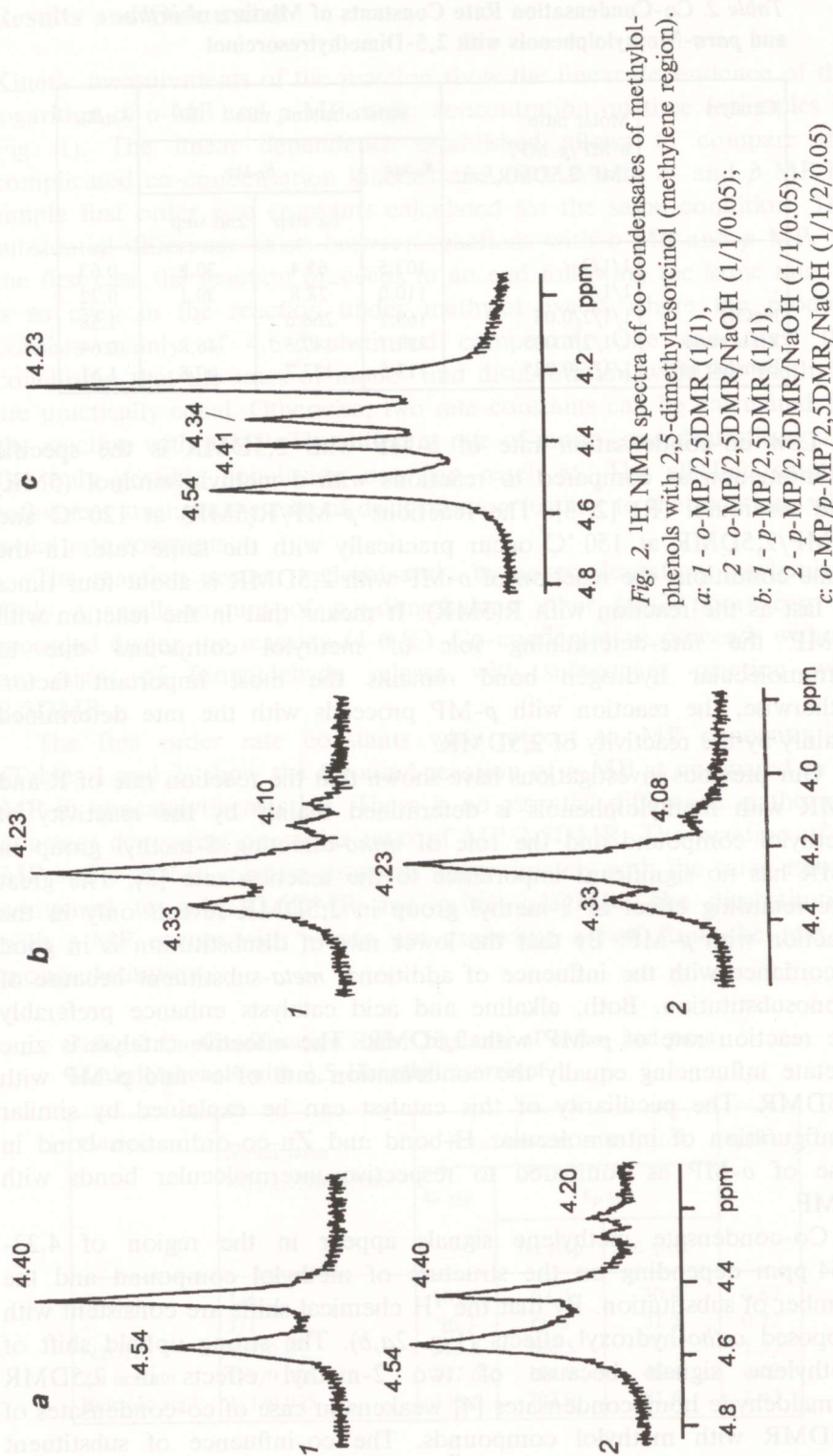


Fig. 2.  $^1\text{H}$  NMR spectra of co-condensates of methylol-phenols with 2,5-dimethylresorcinol (methylene region).

a: 1 - *o*-MP/2,5DMR (1/1),

2 - *o*-MP/2,5DMR/NaOH (1/1/0.05);

b: 1 - *p*-MP/2,5DMR (1/1),

2 - *p*-MP/2,5DMR/NaOH (1/1/0.05);

c: *o*-MP/*p*-MP/2,5DMR/NaOH (1/1/2/0.05)

Table 3. Distribution of Methylene Groups in Methylolphenol - 2,5-Dimethylresorcinol Reaction Products, molar %

Molar ratio		Catalyst	Amount, mole	o-MP/2,5DMR		p-MP/2,5DMR		o-MP/p-MP/2,5DMR			
MP/2,5DMR	o-MP/p-MP/2,5DMR			Type	C4	C4C6	C4	C4C6	o-MP		p-MP
1/1	1/1/2	-	-	54	46	59	35	45	55	52	44
2/1	1/1/1	-	-	6	91	mostly C4C6		~5	~90	~5	~90
1/1	1/1/2	NaOH	0.05	30	65	68	24	34	61	62	33
1/1	1/1/2	Zn acetate	0.005	56	44	61	34	47	53	53	44
1/1	1/1/2	Benzoic acid	0.025	53	47	58	36	47	53	50	45

effects strengthens the downfield shift of methylene signals in case of disubstitution. The spectrum of *o*-MP/*p*-MP/2,5DMR co-condensate consists from the resolved signals assigned already for methylenes in binary systems (Fig. 2c). Most likely the disubstitution of 2,5DMR with different methylol compounds gives methylene signals which coincide with these interpreted for symmetrical disubstituted compounds.

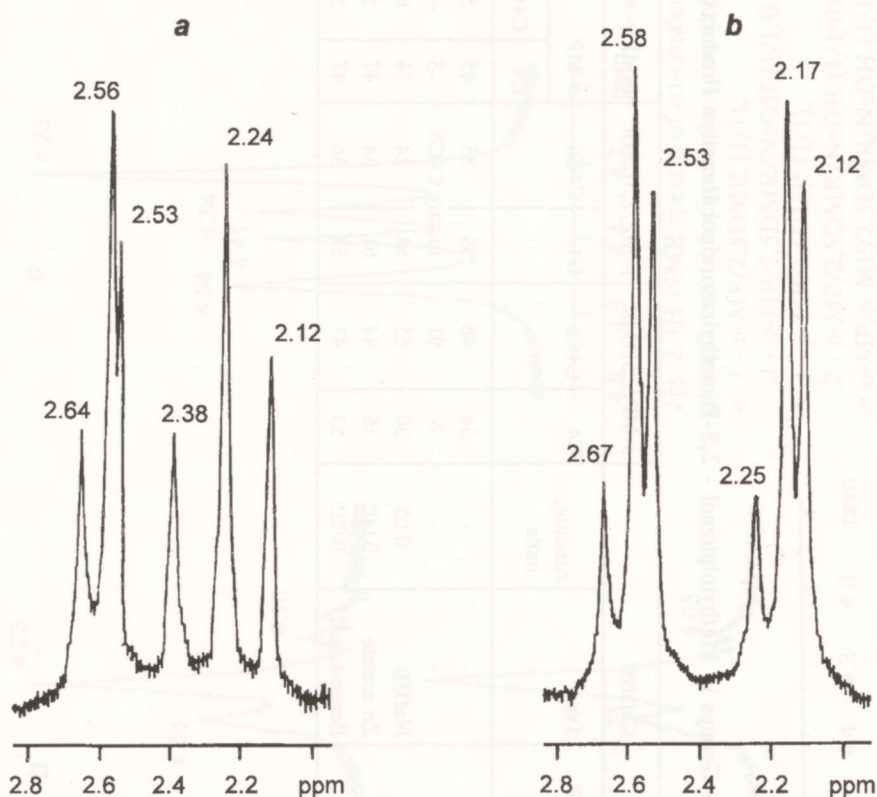


Fig. 3.  $^1\text{H}$  NMR spectra of co-condensates of methylolphenols with 2,5-dimethylresorcinol (methyl region). *a* - *o*-MP/2,5DMR (1/1), 60 min; *b* - *p*-MP/2,5DMR (1/1), 120 min

Using the phenomenon of good resolution of methylene signals, the distribution of methylene groups in MP/2,5DMR reaction products was calculated (Table 3). The products of reaction contain predominantly the co-condensates. The small amount (5-6 %) of *p*-MP self-condensates can be ascertained, mainly with *o,p*-methylenes. The alkaline catalyst promotes slightly the self-condensation giving also in case of *o*-MP/2,5DMR reaction about 5 % of *o,p*-methylenes. The twofold amount of MP easily leads to preferential disubstitution of 2,5DMR. In 1/1 co-condensates the part of C4C6 methylenes depends on methylol compound structure forming 44-47 % in case of *o*-MP and 34-36 % in



case of *p*-MP. NaOH as catalyst has a special influence enhancing or reducing this characteristic depending on *o*-MP or *p*-MP (65 and 24 %, respectively). The co-condensation with *o*-MP/*p*-MP mixture increases the role of disubstituted compounds of 2,5DMR in products.

Because of strong *ortho*-hydroxyl effects C2 methyl group in 2,5DMR gives, in comparison with C5 methyl group, the signal in lower field (2.53 and 2.12 ppm, respectively). The resolution of both signals is sufficient to assign methyl <sup>1</sup>H chemical shifts for free 2,5DMR, 4- and 4,6-substituted compounds (Fig. 3). C2 methyl chemical shifts are quite similar for compounds with both methylols due to the influence of the same hydroxyl effects. The additional *ortho*-hydroxyl effect reveals in downfield shift of C5 methyl signals in compounds with *o*-MP.

## Conclusions

Low co-condensation rate of *para*-methylolphenol with 2,5-dimethylresorcinol as compared to resorcinol or 5-methylresorcinol is the special phenomenon of the studied reaction. 2,5-Dimethylresorcinol acquires the rate-determining role only in the reaction with a *para*-methylol compound. The co-condensation occurs as mono- and disubstitution in 2,5-dimethylresorcinol. The *ortho*-methylol compound and alkaline catalyst promote the disubstitution.

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